

RPR 9140

20-2-55

Japan Patent Office
Public Patent Disclosure Bulletin

Public Patent Disclosure Bulletin No.: 11-352703
Public Patent Disclosure Bulletin Date: December 24, 1999
Request for Examination: Not yet made
Number of Inventions: 10 OL
Total Pages: 8
Int. Cl.6 Identification Code
Internal File Nos.

G 03 F 7/42

C 11 D 1/72

3/04

3/43

7/10

F1 Tech. Indic.

G 03 F 7/42

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Patent Application No.: 10-157791

Patent Application Date: June 5, 1998

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Title of Invention:

Post-ashing treatment solution and treatment method using this solution

Abstract:

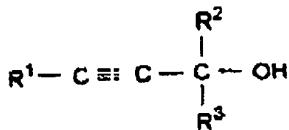
Purpose of Invention: To provide a post-ashing treatment solution for substrates on which dry etching and ashing have been performed under more severe conditions which has the effect of preventing corrosion and excellent ability to remove metal deposition, and does not cause damage even to an organic SOG layer, as well as a method of treatment which uses this solution.

Make-up of Invention: A salt of hydrofluoric acid and a base which does not contain a metal ion are compounded with a water-soluble organic solvent, water, and an acetylene alcohol/alkylene oxide adduct to make a post-ashing treatment solution. Moreover, a substrate is treated by placing a hot-resist pattern on the substrate as a mask and etching and ashing the substrate, after which the aforementioned treatment solution is used to treat it.

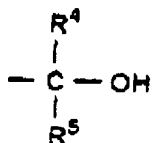
Claims:

- (1) A post-ashing treatment solution in which (a) a salt of hydrofluoric acid and a base which does not contain a metal ion, (b) a water-soluble organic solvent, (c) water, and (d) an acetylene alcohol/alkylene oxide adduct are compounded.
- (2) A post-ashing treatment solution in accordance with Claim (1), in which the acetylene alcohol for forming ingredient (d) is a compound shown by general formula (I) below:

(I)



(where R1 is a hydrogen atom or



and R2, R3, R4, and R5 are each independently hydrogen atoms or C1-6 alkyl groups).

(3) A post-ashing treatment solution in accordance with Claim (1) or Claim (2), in which the alkylene oxide for forming ingredient (d) is ethylene oxide, propylene oxide, or a mixture of them.

(4) A post-ashing treatment solution in accordance with any one of Claims (1)-(3), in which the salt of hydrofluoric acid and a base which does not contain a metal ion (a) is at least one compound selected from a group including hydroxyamines, primary, secondary, or tertiary aliphatic amines, alicyclic amines, aromatic amines, heterocyclic amines, ammonia water, and lower alkyl quaternary ammonium salts.

(5) A post-ashing treatment solution in accordance with any one of Claims (1)-(4), in which ingredient (a) is ammonium fluoride.

(6) A post-ashing treatment solution in accordance with any one of Claims (1)-(5), in which ingredient (a) is at least one compound selected from a group including dimethyl sulfoxide, N,N-dimethyl formamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene

glycol, and diethylene glycol monobutyl ether.

(7) A post-ashing treatment solution in accordance with any one of Claims (1)-(6), in which ingredient (a) is 0.2-30 wt %, ingredient (b) is 30-80 wt %, and the remainder is ingredient (c).

(8) A post-ashing treatment solution in accordance with any one of Claims (1)-(6), in which hydrofluoric acid (e) is also compounded.

(9) A post-ashing treatment solution in accordance with Claim (8), in which ingredient (a) is 0.2-30 wt %, ingredient (b) is 30-80 wt %, ingredient (d) is 0.1-5 wt %, ingredient (e) has an upper limit of 0.5 wt %, and the remainder is ingredient (c).

(10) A treatment method in which a hot-resist pattern is placed on the substrate as a mask and it is etched and ashed, after which a treatment solution mentioned in any one of Claims (1)-(9) is used to treat it.

Detailed Explanation of Invention:

Industrial Field of Application

This invention concerns a post-ashing treatment solution and a treatment method using it. More specifically, it concerns a treatment solution which is excellent for treating substrates on which a hot-resist pattern is placed on the substrate as a mask and dry-etching and ashing are performed, as well as a treatment method which uses this solution. The treatment solution of this invention has a high power of removing hot-resist modified films and metal depositions produced after forming a fine resist pattern and etching and ashing, has an excellent effect of preventing corrosion of metal insulating films deposited by CVD, and prevents the production of damage to organic SOG (spin-on glass) (poisoned bia). This invention is ideal for use in manufacturing semiconductor elements, such as IC or LSI, or liquid crystal panel elements.

Prior Art

Semiconductor elements such as IC or LSI or liquid crystal panel elements are manufactured by uniformly applying a hot resist on a

metal film which has been deposited by CVD on a substrate or an insulating film, such as SiO₂, selectively exposing this film to light, performing a development treatment to form a hot-resist pattern, and selectively etching the substrate on which the aforementioned metal film which was deposited by CVD or insulating film, such as SiO₂, was formed. After fine circuits are formed in this manner, the unneeded hot-resist layer is removed. When the unneeded hot-resist layer is removed, an organic amine stripping solution, which contains organic amines such as monoethanolamine as necessary ingredients, is widely used today, because they have excellent safety and stripping abilities.

Various metal layers deposited by CVD are used, including aluminum (Al); aluminum alloys, such as aluminum-silicon (Al-Si), aluminum-silicon-copper (Al-S-Cu), etc.; titanium (Ti); titanium nitride (TiN); titanium alloys, such as titanium tungsten (TiW), etc.; or tantalum (Ta), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), etc. They are formed on the substrate as single or multiple layers.

With the trend of recent years toward higher densities of integrated circuits, the main type of etching used has become dry etching, which is capable of higher-density fine etching.

Moreover, plasma ashing is performed to remove the unneeded hot-resist layer after the etching. These etching and ashing treatments cause the modified film residue substance to become angular at the sides and bottom of the pattern, or residues from other ingredients will adhere and remain. Furthermore, when the metal film is cut at the time the etching is performed, metal depositions are produced. Therefore, if these are not completely removed, problems such as reduced yield of the semiconductor manufacturing process will be caused.

These residues and depositions have various compositions, depending on the kinds of etching gas used, the ashing conditions, the kinds of metals formed on the substrate, the kinds of insulating films, the kinds of hot resist used, etc. Because of the severity of the treatment conditions in the various kinds of

treatments and the multiplicity of metals, insulating films, and hot resists used, because of various improvements which have been made in semiconductors in recent years, the residues and depositions have become more complex and it is difficult to make sure of which of these compositions one is dealing with, and at present there are no treatment solutions and methods which are completely satisfactory.

In recent years, moreover, there has been a trend towards smoothing by applying a thick organic SOG film layer, instead of using previous etching methods. This organic SOG layer presents the problem that it is easily corroded and damaged by any water in the treatment solution. Therefore, there is increased interest in treatment solutions which also have the effect of preventing damage to the organic SOG layer.

Up to now, hot-resist modified film removal solutions and post-ashing treatment solutions have included, for example, resist stripping solution compositions containing hydrofluoric acid, salts of hydrofluoric acid and bases which do not contain metal ions, water-soluble organic solvents, and preservatives (Japan Public Patent Bulletin No. 8-202052); resist stripping solution compositions containing salts of hydrofluoric acid and bases which do not contain metal ions and water-soluble organic solvents, with a system pH of 5-8 (Japan Public Patent Bulletin No. 9-197681); resist stripping solutions containing acetylene alcohol added to an organic stripping solution (Japan Public Patent Disclosure Bulletin No. 64-73348); etc.

However, although the resist stripping solution compositions of Japan Public Patent Bulletin No. 8-202052 have the property of being able to remove resist modified films and metal depositions after ashing sufficiently well, due to the addition of the hydrofluoric acid, they do not have satisfactory effects in the areas of preventing corrosion of peripheral devices, such as stripping solution feeding devices, preventing damage to organic SOG layers, removing corrosion on metal films and metal oxide films, etc.

The stripping solution compositions of Japan Public Patent Bulletin No. 9-197681 were proposed as improvements of the technology of the patent mentioned above. That is, since it was discovered that the corrosion of the peripheral devices and the ability to remove metal depositions in the technology of this invention are due to the pH in the stripping solution composition system being inclined toward the acidic side (when too much hydrofluoric acid is compounded with the other ingredients), the quantity of the hydrofluoric acid in the composition was decreased and made a minute quantity. However, even though this stripping solution composition also suppresses corrosion of metal films, metal oxide films, peripheral devices, etc., and damage to the organic SOG layer, it is not completely satisfactory in removing residues when fine patterns are formed.

Furthermore, the stripping solution mentioned in Japan Public Patent Disclosure Bulletin No. 64-73348 is used in hot resist stripping treatments in manufacturing technologies which do not include ashing processes, and cannot be used effectively for removing hot-resist modified films or metal depositions under severe etching and ashing conditions in the formation of fine patterns, as is done presently.

Problems That the Invention Is to Solve

This invention was made with the situation described above in mind; its purpose is to provide a post-ashing treatment solution which has an excellent ability to treat substrates on which dry etching and ashing have been performed under more severe conditions and an excellent effect of preventing corrosion on substrates on which conductive metal layers have been formed, as well as a method of treatment which uses this treatment solution. The treatment solution of this invention has an especially good ability to remove metal depositions from substrates on which fine patterns have been formed, and also prevents corrosion of metal films and metal oxide films. In addition, it does not damage organic SOG layers.

Means of Solving These Problems

The inventors performed careful investigations concerning ways of preventing the effects of hydrofluoric acid as much as possible, considering that, with conventional treatment solutions containing hydrofluoric acid, if the hydrofluoric acid content is reduced sufficient removal of residues is not obtained, but if the content of hydrofluoric acid is increased the problems of corrosion of metal layers or metal oxide layers and damage to the organic SOG layer is caused, so that it is difficult to strike a balance. As a result, they discovered that these problems could be solved by adding specific compounds to a treatment solution containing a water-soluble organic solvent, a salt of hydrofluoric acid and a base which does not contain a metal ion, and water. Thus, they perfected this invention.

That is, this invention concerns a post-ashing treatment solution in which (a) a salt of hydrofluoric acid and a base which does not contain a metal ion, (b) a water-soluble organic solvent, (c) water, and (d) an acetylene alcohol/alkylene oxide adduct are compounded.

Form of Embodiment of This Invention

This invention will be explained in more detail below.

In the salt of hydrofluoric acid and a base which does not contain a metal ion of ingredient (a), examples of desirable bases which do not contain metal ions are hydroxylamines, primary, secondary, or tertiary aliphatic amines, alicyclic amines, aromatic amines, heterocyclic amines, ammonia water, and lower alkyl quaternary ammonium salts.

Specific examples of these hydroxylamines are hydroxylamine (NH_2OH), N-methylhydroxylamine, N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine, etc.

Specific examples of these primary aliphatic amines are monoethanolamine, ethylenediamine, 2-(2-aminoethyl)ethanol, etc.

Specific examples of these secondary aliphatic amines are diethanolamine, dipropylamine, 2-ethylaminoethanol, etc.

Specific examples of these tertiary aliphatic amines are

dimethylaminoethanol, ethyldiethanolamine, etc.

Specific examples of these alicyclic amines are cyclohexylamine, dicyclohexylamine, etc.

Specific examples of these aromatic amines are benzylamine, dibenzylamine, N-methylbenzylamine, etc.

Specific examples of these heterocyclic amines are pyrrole, pyrrolidine, pyrrolidone, pyridine, morpholine, pyrazine, piperidine, N-hydroxyethylpiperidine, oxazole, thiazole, etc.

Specific examples of these lower alkyl quaternary ammonium salts are tetramethylammonium hydroxide (=TMAH), tetraethylammonium hydroxide, tetrapropylammonium hydroxide, trimethylethylammonium hydroxide, (2-hydroxyethyl)trimethyl ammonium hydroxide, (2-hydroxyethyl)triethylammonium hydroxide, (2-hydroxyethyl)tripropylammonium hydroxide, (1-hydroxypropyl)trimethylammonium hydroxide, etc.

Among these, ammonia water, monoethanolamine, tetramethylammonium hydroxide, and (2-hydroxyethyl)trimethylammonium hydroxide are desirable for use, since they are easily obtainable and have excellent safety.

The bases not containing metal ions may be used individually or in combinations of 2 or more.

These salts of bases not containing metal ions and hydrofluoric acid can be manufactured by adding the bases not containing metal ions to commercial hydrofluoric acid, with a hydrogen fluoride concentration of 50-60%, so that the pH becomes about 5-8. As this kind of salt, ammonium fluoride is the most desirable.

In the treatment solution of this invention, the upper limit of the quantity of ingredient (a) should be 30 wt %, especially 20 wt %. The lower limit should be 0.2 wt %, preferably 0.5 wt %.

As the water-soluble organic solvent which is ingredient (b), one can use water or an organic solvent which is miscible with the other ingredients of this invention.

Examples of these water-soluble organic solvents are sulfoxides, such as dimethylsulfoxide; sulfones, such as dimethylsulfone, diethylsulfone, bis(2-hydroxyethyl)sulfone, tetramethylenesulfone,

etc.; amides, such as N,N-dimethylformamide, N-methylformamide, N,N-dimethylacetoamide, N-methylacetoamide, N,N-diethylacetoamide, etc.; lactams, such as N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, N-propyl-2-pyrrolidone, N-hydroxymethyl-2-pyrrolidone, N-hydroxyethyl-2-pyrrolidone, etc.; imidazolidinones, such as 1,3-dimethyl-2-imidazolidinone, 1,3-diethyl-2-imidazolidinone, 1,3-diisopropyl-2-imidazolidinone, etc.; lactones, such as γ -butyrolactone, δ -valerolactone, etc.; polyhydric alcohols, such as ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, etc.; and derivatives of these compounds. These solvents may be used individually or in combinations of 2 or more. Among these solvents, dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetoamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and diethylene glycol monobutyl ether are desirable, since they have an excellent ability to strip modified films. Among these solvents, dimethylsulfoxide is especially desirable, since it has a superior corrosion-preventing effect on substrates. The upper limit of the quantity of ingredient (b) compounded in the treatment solution of this invention should be 80 wt %, especially 70 wt %. The lower limit should be 30 wt %, especially 40 wt %. The water of ingredient (c) is necessarily contained in ingredient (b) but more water is compounded in this invention. Furthermore, as ingredient (d) in the treatment solution of this invention, an acetylene alcohol/alkylene oxide adduct, in which an alkylene oxide is added to an acetylene alcohol, is compounded. Desirable examples of these acetylene alcohols are ones shown by general formula (I) below:

(I)

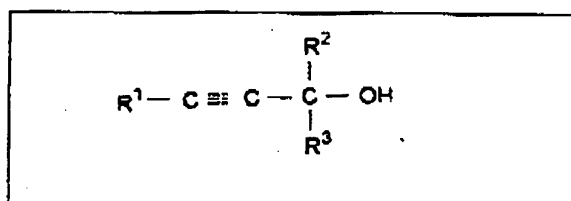
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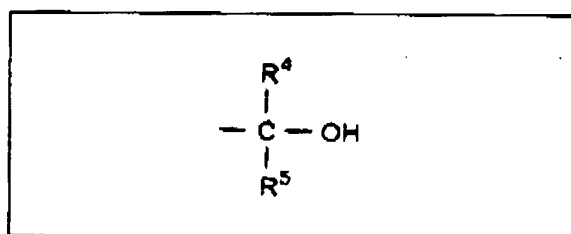
etc.; amides, such as N,N-dimethylformamide, N-methylformamide, N,N-dimethylacetoamide, N-methylacetoamide, N,N-diethylacetoamide, etc.; lactams, such as N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, N-propyl-2-pyrrolidone, N-hydroxymethyl-2-pyrrolidone, N-hydroxyethyl-2-pyrrolidone, imidazolidinones, such as 1,3-dimethyl-2-imidazolidinone, 1,3-diethyl-2-imidazolidinone, 1,3-diisopropyl-2-imidazolidinone, etc.; lactones, such as g-butyrolactone, d-valerolactone, ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether, etc.; and derivatives of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether, etc.; and derivatives of monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, etc. Among these solvents, these compounds of 2 or more. Among these solvents, combinations of 2 or more. Among these solvents, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, ethylene glycol, and diethylene glycol monoethyl ether are desirable, since they have an excellent ability to strip modified films. Among these solvents, dimethylsulfoxide, N,N-dimethylacetoamide, it has a superior corrosion-preventing effect on substrates. The upper limit of the quantity of ingredient (b) compounded in the treatment solution of this invention should be 80 wt %, especially 70 wt %. The lower limit of this invention should be 30 wt %, especially 40 wt %. The water of ingredient (c) is necessarily contained in ingredient (b) but more water is compounded in this invention. Furthermore, an acetylene alcohol/alkylene oxide adduct, in which an alkylene oxide is added to an acetylene alcohol, is compounded. Desirable examples of these acetylene alcohols are ones shown by general formula (I) below:

(I)

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(where R₁ is a hydrogen atom or

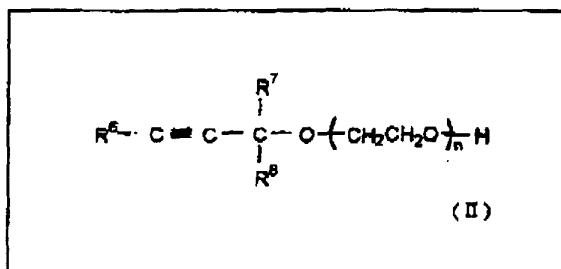


and R₂, R₃, R₄, and R₅ are each independently hydrogen atoms or C1-6 alkyl groups). Here, examples of the C1-6 alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, isohexyl, 3-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, etc., groups.

Ideal acetylene alcohols of this kind are, for example, those sold as the series "Surfinol" [saafinooru], "Olfin" [orufin], etc. (all produced by Air Products and Chemicals Inc.). Among these, Surfinol 104, Surfinol 82 or mixtures of them are the most desirable for use. Other ones which can be used are Olfin B, Olfin P, Olfin Y, etc.

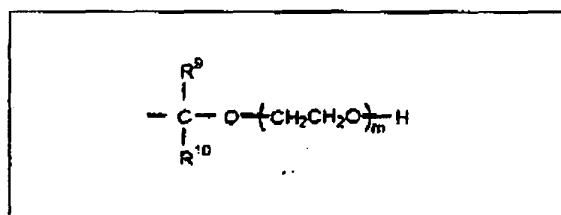
As the alkylene oxide added to the af/ acetylene alcohol, it is desirable to use ethylene oxide, propylene oxide, or a mixture of them.

In this invention, cd/s shown by the general formula (II)



(II)

(where R6 is a hydrogen atom or



and R7, R8, R9, and R10 are each independently hydrogen atoms or C1-6 alkyl groups) are desirable for use as ingredient (d). Here, (n+m) is an integer in the range of 1-30; the properties such as solubilities in water and surface tension vary to a very slight degree due to the addition number of the ethylene oxide. The substances of ingredient (d) are themselves well known as surface active agents. They are sold as the series "Surfinol" (produced by Air Products and Chemicals Inc.) or "Acetylenol" [asechirenooru] (produced by Kawaken Fine Chemicals Co.). Among these, considering properties such as solubility in water and surface tension, which are due to the addition number of the ethylene oxide, ideal ones are Surfinol 440 (n+m=3.5), Surfinol 465 (n+m=10), Surfinol 485 (n+m=30), Acetylenol EL (n+m=4), Acetylenol EH (n+m=10), or mixtures of them. Mixtures of Acetylenol EL and Acetylenol EH are especially desirable. Among these, a mixture of Acetylenol EL and Acetylenol EH in the proportions of 2:8-4:6 (weight ratio) is especially ideal.

In this invention, by compounding ingredient (d), the permeability and wettability of the treatment solution itself can be increased; when a hole pattern, etc., is formed, the contact area with the pattern side surface becomes larger. By this means, it appears, the ability to remove metal deposition produced on the bottom of the pattern is increased.

In the treatment solution of this invention, the upper limit of the quantity of ingredient (d) compounded should be 5 wt %, especially 2 wt %, and the lower limit should be 0.1 wt %, especially 0.15 wt %. When it is larger than this range, the production of gas bubbles is considered and the increase of wettability is saturated, so that no further increase in the effect is looked for; on the other hand, if it is smaller than this range, a sufficient effect of the wettability looked for is difficult to obtain.

In the treatment solution of this invention, one can also add hydrofluoric acid as ingredient (e). This ingredient (e) can be compounded in a range such that the pH can be kept near neutrality (about 5-8). The optimum quantity in this case is at most 0.5 wt %. If the quantity of ingredient (e) added is greater than this, the acidity of the treatment solution will become too strong and corrosion of the metal or metal oxide film will become severe, which is not desirable. If the quantity of ingredient (e) is lower than 0.1 wt %, the corrosion of the metal or metal oxide film is kept especially low and an excellent removal ability, which is the essential purpose of this treatment solution, will be obtained; therefore, this is desirable.

Furthermore, if desired, one can compound a corrosion-preventing agent with the treatment solution of this invention. The corrosion-preventing agent used may be selected at will from conventional organic amine stripping solutions. In particular, it is desirable to use at least one compound from a group including aromatic hydroxy compounds, acetylene alcohols, organic compounds containing carboxyl groups and their anhydrides, triazole compounds, and similar compounds.

The post-ashing treatment solutions of this invention can be used advantageously for photoresists which can be developed by alkaline aqueous solutions, including negative or positive photoresists. Examples of such photoresists are (i) positive photoresists containing naphthoquinone diazide compounds and novolak resins, (ii) positive photoresists which contain compounds which produce acids by exposure to light, compounds which increase in solubility in alkaline aqueous solutions when decomposed by acids, and alkali-soluble resins; (iii) positive photoresists which contain compounds which produce acids by exposure to light and alkali-soluble resins which have groups which increase in solubility in alkaline aqueous solutions when decomposed by acids; and (iv) negative photoresists which contain compounds which produce acids due to light, cross-linking agents, and alkali-soluble resins. However, the photoresists are not limited to these kinds.

The method of treatment of this invention is one in which a substrate is treated by placing a hot-resist pattern on the substrate as a mask and etching and ashing the substrate, after which the aforementioned treatment solution is used to treat it. Specifically, a photoresist layer is formed on a substrate such as a silicon wafer, glass, etc. If desired, a conductive metal film or metal oxide film, or an insulating film such as SiO_2 , is formed on the substrate by deposition, etc. Examples of the aforementioned conductive metal films or metal oxide films are aluminum (Al); aluminum alloys, such as aluminum-silicon (Al-Si), aluminum-silicon-copper (Al-S-Cu), etc.; titanium (Ti); titanium nitride (TiN); titanium alloys, such as titanium tungsten (TiW), etc.; or tantalum (Ta), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), etc. They are formed on the substrate as single or multiple layers. In particular, the treatment solution of this invention can exhibit especially great effectiveness on Al; Al-Si, Al-Si-Cu, and other Al alloys; Ti: TiN, TiW, and other Ti alloys; this is because, when the treatments mentioned above are performed, residues adhere to these substrates, and deposition

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is easily produced. Next, a photoresist pattern is formed. The light exposure and development conditions can be selected as is suitable for the photoresist used. The light exposure may be performed, for example, by sources of ultraviolet light or far infrared light, excimer lasers, or light sources producing X-rays, electron beams, or other active light rays. Examples of such light sources are low-pressure mercury lamps, high-pressure mercury lamps, ultra-high-pressure mercury lamps, xenon lamps, etc. The photoresist layer is exposed through the desired mask pattern or electron beam. After this, if desired, a post-exposure heat treatment (post-exposure bake) is performed. Next, a specific photoresist pattern can be obtained by performing pattern development using a photoresist developer, and the specific photoresist pattern is obtained. The development method is not especially limited; one can use various development processes depending on the purpose one has. For example, one can use immersion development, in which the substrate with the photoresist applied is immersed in the developer for a specific time and then washed and dried; paddle development, in which the developer is dropped on the applied photoresist surface and this is left standing for a specific time, after which it is washed with water and dried; or spray development, in which the developing solution is sprayed on the photoresist surface and then washed with water and dried. Next, etching is performed on the aforementioned conductive metal mask, etching is performed by selective dry etching, etc., and a fine circuit is formed. After this, the unneeded photoresist layer is removed by plasma ashing. At this time, resist residue after the ashing or metal deposition produced during the metal film etching adheres and remains on the substrate surface. These residues are put into contact with the treatment solution of this invention and are removed. They can be easily removed by using the treatment

solution of this invention. It is especially effective in preventing corrosion on substrates containing metals, such as Al and Al alloys.

Moreover, the treatment solution of this invention also has the effect of preventing damage to substrates with organic SOG layers on them, and does not perform etch-back.

Working Examples

Next, this invention will be explained in further detail by giving working examples, but it is not at all limited by these examples. Unless otherwise specified, the quantities compounded are shown as wt %.

Working Examples 1-6, Comparison Examples 1-4

An Al-Si-Cu layer approximately 400 nm thick was formed as the first layer on a silicon wafer, followed by a Ti layer approximately 30 nm thick as the second layer, a TiN layer of approximately 30 nm as the third layer, an SiO₂ layer approximately 300 nm thick, formed by plasma CVD, as the fourth layer, an organic SOG layer approximately 400 nm thick as the fifth layer, and an SiO₂ layer approximately 500 nm thick, formed by plasma CVD, as the sixth layer. A positive photoresist THMR-IP3300 consisting of a naphthoquinone diazide compound and a novolak resin (Tokyo Oka Kogyo Co.) was applied by means of a spinner, and pre-baking was performed for 90 minutes at 90°C; a photoresist layer 0.2 mm thick was formed. This photoresist layer was exposed through a mask pattern, using an NSR-200510D (Nikon Co.), and a development treatment was performed by using a 2.38 wt % tetramethylammonium hydroxide (TMAH) to obtain the photoresist pattern. Next, post-baking was performed for 90 seconds at 120°C. Next, using the etching device TSS-6000 (Tokyo Oka Kogyo Co.), this substrate was etched by using a mixed gas of hydrochloric acid and boron trichloride as the etchant, for 168 seconds under a pressure of 5 mm torr and at a stage temperature of 20°C. Next, an after-corrosion treatment (a treatment removing the chlorine atoms) was performed for 30 seconds, under a pressure of 20 mm

torr and at a stage temperature of 20°C, using a mixed gs of oxygen and trifluoromethane. Next, an ashing treatment was performed on the hot resist pattern for 40 seconds, under a pressure of 1.2 mm torr and at a stage temperature of 220°C, using an ashing device TCA-3822 (Tokyo Oka Kogyo Co.).

Using this treated substrate, the metal deposition removal ability, corrosion of metal and metal oxide layers, and damage to the organic SOG layer were evaluated by the evaluation methods and criteria described below. The results are shown in Tables 1 and 2. Furthermore, there were no great differences among the examples in the removal of the photoresist modified film.

Evaluations performed:

Ability to remove metal depositions: The aforementioned treated substrate was immersed in treatment solutions with the compositions shown in Tables 1 and 2 for 5 minutes at 23°C to perform metal deposition removal treatments. The treated substrate was put through a rinse treatment with pure water and the residue of metal deposition was examined by SEM (scanning electron microscope) photography. Evaluation was performed according to the following standards:

- O: Metal deposition completely removed
- [Delta]: Some metal deposition remained
- X: Considerable metal deposition remained

Corrosion of metal or metal oxide films: The aforementioned treated substrate was immersed in treatment solutions with the compositions shown in Tables 1 and 2 for 10 minutes at 23°C. After the substrate was lifted from the treatment solution, the state of corrosion of the metal or metal oxide film was examined by SEM (scanning electron microscope) photography. If there was no corrosion, the evaluation was "O"; if corrosion occurred, the evaluation was "X".

Damage to organic SOG layer: The aforementioned treated substrate was immersed in treatment solutions with the compositions shown in Tables 1 and 2 for 10 minutes at 23°C. After the substrate was lifted from the treatment solution, the state of damage to the organic SOG layer was examined by SEM (scanning electron microscope) photography. If there was no damage, the evaluation was "O"; if damage occurred, the evaluation was "X".

Table 1

Table 1						
Composition	Working Ex. 1	Working Ex. 2	Working Ex. 3	Working Ex. 4	Working Ex. 5	Working Ex. 6
Antimony fluoride	1	1	1	1	1	1
Hydrofluoric acid	0	0	0	0	0	0
Acetylene alcohol/styrene oxide adduct	0.1	0.2	0.2	0.2	1	3
Water	30	30	30	30	30	30
Water-soluble organic solvent (methanol)	DMSO	DMF	NMP	DMSO	DMSO	DMSO
Ability to remove metal deposition	Δ	O	O	O	O	O
Corrosion of metal/metal oxide film	O	O	O	O	O	O
Damage to organic SOG layer	O	O	O	O	O	O

Table 2

Table 2				
Composition	Comparison Ex. 1	Comparison Ex. 2	Comparison Ex. 3	Comparison Ex. 4
Ammonium fluoride	1	1	1	1
Hydrofluoric acid	0.05	0	0	0
Acetylene alcohol/alkylene oxide adduct	0	0	0	0
Water	30	30	30	30
Water-soluble organic solvent (remainder)	DMSO	DMSO	DMSO	DMSO
Ability to remove metal deposition	0	x	x	x
Corrosion of metal/metal oxide film	x	0	0	0
Damage to organic SOG layer	x	0	0	0

In Tables 1 and 2, "DMSO" refers to dimethylsulfoxide, "DMF" to N,N-dimethylformamide, and "NMP" to N-methyl-2-pyrrolidone. The acetylene alcohol/alkylene oxide adduct used was a mixture of Acetylenol EL and Acetylenol EH in the weight ratio of 3:7.

Working Example 7

The photoresist pattern formation, etching treatment, and ashing treatment were performed in the same manner as in Working Examples 1-6, except that an Al-Si-Cu layer approximately 400 nm thick, was formed as the first layer on a silicon wafer, followed by a Ti layer approximately 30 nm thick as the second layer, a TiN layer of approximately 30 nm as the third layer, and an SiO₂ layer approximately 300 nm thick, formed by plasma CVD, as the fourth layer. A treated substrate was obtained as the result.

This treated substrate was immersed for 5 minutes at 23°C in a treatment solution consisting of 1 wt % ammonium fluoride, 0.1 wt % acetylene alcohol/alkylene oxide adduct [mixture of Acetylenol

EL:Acetylenol EH=3:7 (weight ratio)], 30 wt % water, 0.05 wt % hydrofluoric acid, and the remainder DMSO. The treated substrate was rinsed with pure water and the residual metal deposition was examined by SEM (scanning electron microscope) photography. It was found that the metal deposition was completely removed.

This treated substrate was also immersed in the aforementioned treatment solution for 10 minutes at 23°C, and after it was lifted from the treatment solution, the state of corrosion of the metal/metal oxide film was examined by SEM (scanning electron microscope) photography; no corrosion was found.

Effects of Invention

As discussed above in detail, this invention provides a post-ashing treatment solution for substrates on which dry etching and ashing have been performed under more severe conditions which has an excellent effect of preventing corrosion of substrates on which conductive metal layers have been formed, as well as a method of treatment which uses this solution. The treatment solution of this invention is an excellent method for removing metal deposition on substrates on which fine patterns have been formed. Furthermore, it does not damage substrates on which organic SOG layers are formed.

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Int. Cl.6

Identification Code

Internal File Nos.

G 03 F 7/42

C 11 D 7/22

7/50

H 01 L 21/306

// H 01 L 21/027

F1 Tech. Indic.

C 11 D 7/22

7/50

H 01 L 21/302 H

21/30 572 B

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